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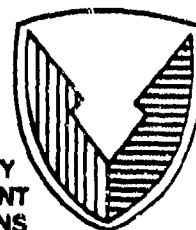
**THE CHEMICAL FATE OF BRASS DUST
IN WATERS OF VARYING HARDNESS LEVELS**

**William T. Muse, Jr.
RESEARCH DIRECTORATE**

August 1988

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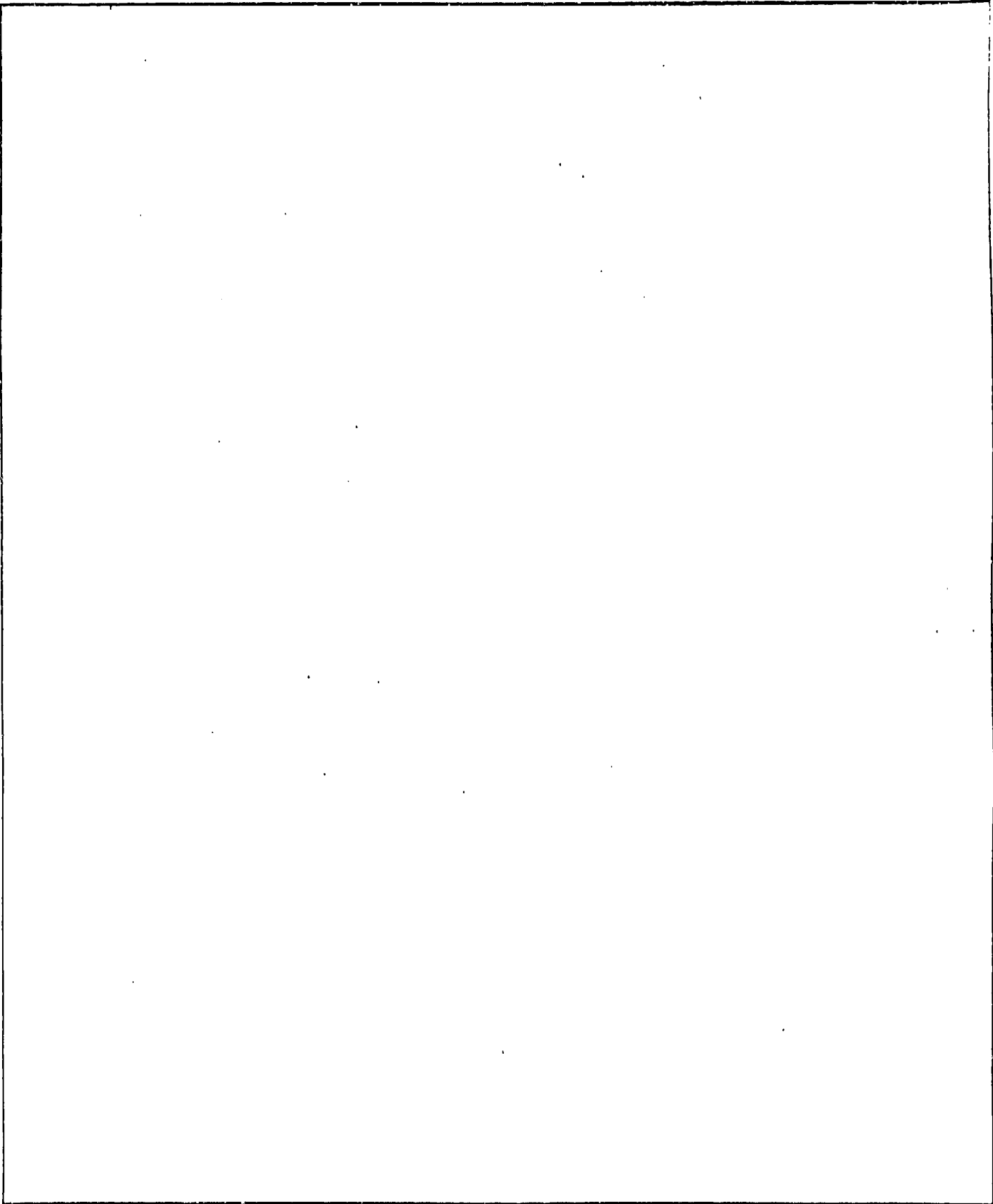
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PREFACE

The work described in this report was authorized under Project No. 1L162622A552, Smoke/Obscurant Systems, and funded as job order 5N68-01-002 under the Environmental Fate and Effects Program at the U.S. Army Chemical Research, Development and Engineering Center. This work was started in August 1984 and completed in February 1986. The experimental data are recorded in laboratory notebooks 84-0059, 84-0171, and 85-0096.

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This report has been approved for release to the public.

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CONTENTS

	Page
1. INTRODUCTION.....	7
2. MATERIALS AND METHODS.....	8
2.1 Preparation of Reconstituted Water.....	8
2.2 Preparation and Chemical Analysis of Brass Powder.....	8
2.3 Preparation of Brass Test Samples (Surface Versus Sonicated Application).....	9
2.4 Chemical Analysis of Brass in Waters of Varying Hardness Levels.....	10
3. RESULTS.....	12
4. DISCUSSION.....	23
5. CONCLUSIONS.....	25
LITERATURE CITED.....	27

LIST OF FIGURES

Figure No.	Page
1 Brass Dissociation (Surface) Soluble Cu vs. Water Hardness.....	13
2 Brass Dissociation (Sonicated) Soluble Cu vs. Water Hardness.....	14
3 Brass Dissociation (Surface) Soluble Zn vs. Water Hardness.....	15
4 Brass Dissociation (Sonicated) Soluble Zn vs. Water Hardness.....	16

5	Surface Applied vs. Sonicated Brass Soluble Cu - Soft Water.....	17
6	Surface Applied vs. Sonicated Brass Soluble Zn - Very Hard Water.....	18
7	Dissociation of Brass vs. Grenade Soluble Metal in Soft Water.....	19
8	Kinetic Rate Determination of Zn Leaving the Brass in Very Soft Water.....	21

LIST OF TABLES

Table No.		Page
1	Quantities of Reagent-Grade Chemicals Required to Prepare Recommended Reconstituted Fresh Waters and the Resulting Water Qualities.....	9
2	Experimental Design: Number of Replicate Samples per Hardness Level for Brass Dust and Grenade Launched Brass. Both Surface and Sonicated Applications Consisted of Five Replicates.....	11
3	First-Order, Kinetic Approximations of Soluble Cu and Zn Leaving the Brass.....	22

THE CHEMICAL FATE OF BRASS DUST IN WATERS OF VARYING HARDNESS LEVELS

1. INTRODUCTION

This study was conducted to assess the environmental fate of brass dust in aquatic systems by examining the dust's rate of decomposition in waters of varying hardness levels. The brass dust consists of approximately 70% copper (Cu) and 30% zinc (Zn). It has the consistency of a fine powder with an average particle diameter ranging from 1 to 6 μm and a mean thickness from 1300-3500 \AA .¹ The U.S. Army is considering using the brass as an infrared smoke to screen troop or vehicle movements. A cloud of this smoke released into the environment could eventually find its way into aqueous systems, either by direct application onto the water surface or by transport mechanisms within nature (e.g., as wind and runoff). This deposition of heavy metals could have a negative impact on aquatic organisms.^{2,3,4}

The toxicity of brass dust on aquatic organisms may involve its dissociation into soluble Cu and Zn or its ingestion by marine organisms. The toxicity of soluble metals, particularly Cu, to aquatic organisms has been well documented with low concentrations (0.1 to 1.0 mg/L Cu) causing toxic effects to many species of freshwater algae.² Results from studies on the acute exposure of microalgae to brass dust indicate that concentrations of 0.06 to 0.32 mg/L brass can decrease the organisms' biomass by 50%.³ Soluble Cu levels during this experiment ranged from 0.04 mg/L Cu at the low dose, up to 1.3 mg/L Cu at the high dose, indicating a significant dissociation of Cu from the brass. Results from studies on the acute exposure of *Daphnia magna* to brass dust show an EC_{50} of 23 $\mu\text{g/L}$ Cu.⁴ Microscopic examination of the daphnid gut revealed the presence of ingested brass particles. These particles were deemed responsible for the reported toxicity.

Various conditions cause brass to dissociate into Cu and Zn in an aqueous system. Primary environmental factors include pH, temperature, salinity, water velocity, wind, organic matrix, and hardness. Many of these factors work in conjunction with one another to determine the rate of brass corrosion.⁵ The most common brass corrosion products predicted by Evans are the Cu oxides CuO , Cu_2O , and the Zn oxide/hydroxide ZnO/Zn(OH)_2 .⁵

The hardness level is one of the important characteristics of natural waters. Hardness is defined as the concentration of all metallic cations (except those of the alkali metals) present in water.⁶ Generally, hardness is a measure of the concentration of calcium (Ca) and magnesium (Mg) ions in water and is frequently expressed as milligrams per liter of carbonate (CaCO_3) equivalent.⁶ Natural waters vary in their hardness levels from very soft (10 mg/L CaCO_3) to very hard (>280 mg/L CaCO_3). The level of water hardness can affect the degree of metal solubility in an aqueous system due to the carbonate complexing of metal ions.

This study examined the chemical fate of brass in waters of varying hardness levels by monitoring the levels of soluble Cu and Zn dissociated from the brass. In addition to hardness levels, metal dissociation was also examined in waters of varying hardness where the brass was applied only on the water surface, as opposed to mixing the brass into the water. This application simulated the initial introduction of brass dust onto a water surface versus its subsequent mixing into the water column due to the effects of wind and current.

2. MATERIALS AND METHODS

2.1 Preparation of Reconstituted Water.

Test water samples were adjusted to the desired hardness level by dissolving specific quantities of salts into deionized water (Table 1). Very soft (10 mg/L), soft (45 mg/L), hard (156 mg/L), and very hard (316 mg/L) levels were prepared. The total hardness concentration (as CaCO_3) of each level was determined by EDTA titration with Eriochrome Black T indicator.⁷ Environmental Protection Agency (EPA) quality assurance samples for hardness were run concurrently with test samples to ensure true hardness values. Sample pH for each hardness level ranged from 7.4 (very soft) to 8.3 (very hard). Preliminary tests conducted by this investigator indicated that this pH range would not adversely affect the dissociation rate of the brass. The subsequent addition of brass to the reconstituted water samples did not affect the hardness or pH levels.

2.2 Preparation and Chemical Analysis of Brass Powder.

Two types of brass powder were used for this study. The first type consisted of the brass dust received directly from

Table 1. Quantities of Reagent-Grade Chemicals Required to Prepare Recommended Reconstituted Fresh Waters and the Resulting Water Qualities.

Name	Salts required (mg/L)				pH	Predicted	
	NaHCO ₃	CaSO ₄ ·2H ₂ O	MgSO ₄	KCl		Hardness (mg/L as CaCO ₃)	Alkalinity (mg/L as CaCO ₃)
Very soft	12	7.5	7.5	0.5	6.4-6.8	10-13	10-13
Soft	48	30.0	30.0	2.0	7.2-7.6	40-48	30-35
Hard	192	120.0	120.0	8.0	7.6-8.0	160-180	110-120
Very hard	384	240.0	240.0	16.0	8.0-8.4	280-320	225-245

¹From "Methods for Acute Toxicity Tests with Fish, Macroinvertebrates, and Amphibians," EPA 660/3-75-009, 1975.

the manufacturer. The second type consisted of the same brass after it had been disseminated from an M76 smoke grenade. Because the grenade-brass would be released into the environment, it was important to measure and compare the metal dissociation from this material as well as the original brass.

Prior to their addition into reconstituted water, the brass and grenade powder were conditioned to remove any surface moisture and analyzed for their Cu and Zn decomposition products. Conditioning consisted of oven drying (70 °C) overnight and storage in a desiccator until weighing. Aliquots of both brass materials were then weighed (0.1 g), digested with nitric acid, and analyzed by flame atomic absorption (AA) spectroscopy. The brass consisted of 66 ± 1% Cu and 26 ± 2% Zn. The grenade brass consisted of 62 ± 0.2% Cu and 23.7 ± 0.1% Zn.

2.3 Preparation of Brass Test Samples (Surface Versus Sonicated Application).

Testing on the manufactured brass was conducted at all four hardness levels, whereas the grenade brass was tested on the soft and hard water only. In both tests, the conditioned brass was weighed (2.0 mg ± 0.1 mg) on a Cahn 28 electrobalance, then transferred to the reconstituted water. One set of water samples consisted of applying the brass only on the water surface layer (static test); the second set consisted of mixing the brass by sonication into the water (sonic tests). For surface applications, the brass was quantitatively transferred into a

250-mL polycarbonate flask by successive rinses with the specific test water. Each sample was then diluted to 200 mL to give an effective concentration of 10.0 mg/L of brass powder. For sonic tests, the brass was first quantitatively transferred into a 20-mL polycarbonate test tube where the brass was vigorously shaken and sonicated until it was thoroughly mixed within the test tube. This mixture was then transferred and diluted into a 250-mL polycarbonate flask to give the same brass concentration level as the surface samples.

Altogether, six replicate samples were prepared at each hardness level for both surface and sonicated applications (Table 2). Samples 1-5 were analyzed for dissolved metal on days 0, 1, 3, 7, 14, and 21 after the addition of brass. Sample 6 was analyzed on day 21 only. This analysis was to determine if any significant change in dissolved ion concentration would occur due to sequential sample withdrawal for analysis of each of the five replicates. Sample 6 was also analyzed for total metal concentration (dissolved and undissolved) following the 21-day test period.

2.4 Chemical Analysis of Brass in Waters of Varying Hardness Levels.

Surface and sonicated brass samples were analyzed for dissolved Cu and Zn by AA spectroscopy. The dissolved metals in the surface samples were measured by inserting the AA aspiration tube directly into the sample water approximately 1 to 2 in. beneath the surface water layer. A comparison of filtered versus nonfiltered samples showed that filtering was not required to obtain the dissolved metal concentration of the surface applied brass samples. Sonicated samples had the brass thoroughly mixed within the water column; therefore, these samples had to be filtered prior to AA analysis. Sample aliquots were drawn up into a 10-mL Teflon-bore syringe. The syringe was then connected to a 25-mm filter holder, and the sample was filtered through a prewashed 0.45- μ m filter (Millipore) to separate dissolved from suspended metals.

Quality assurance of the metal levels in the test samples was verified by analyzing sample blanks and spiked water samples. Metal background levels were monitored by analyzing each type of water hardness without adding brass. Typically, these levels were below the analytical sensitivity for the monitored metals; therefore, no metal interference from the reconstituted

Table 2. Experimental Design: Number of Replicate Samples per Hardness Level for Brass Dust and Grenade Launched Brass. Both Surface and Sonicated Applications Consisted of Five Replicates.

Table 2. Experimental Design: Number of replicate samples per hardness level for brass dust and grenade launched brass. Both surface and sonicated applications consisted of five replicates.

BRASS (surface and sonicated)				
	Very Soft	Soft	Hard	Very Hard
Day 0	5	5	5	5
Day 1	5	5	5	5
Day 3	5	5	5	5
Day 7	5	5	5	5
Day 14	5	5	5	5
Day 21	6	6	6	6

GRENADE BRASS (surface and sonicated)		
	Soft	Hard
Day 0	5	5
Day 1	5	5
Day 3	5	5
Day 7	5	5
Day 14	5	5
Day 21	6	6

water could occur. Each level of water hardness was also spiked with commercial AA standards and adjusted to a basic pH to monitor the fate of soluble Cu and Zn under test conditions. Results of the spiked samples showed that soluble Cu and Zn levels did not change due to the basic pH.

3. RESULTS

The concentration of dissolved metal (milligrams per liter) dissociated from the brass was plotted against time (days) to show the extent of metal solubility and equilibration time at each hardness level (Figures 1-4). The percentage of dissociation of the brass, shown on the right side (y-axis) of each graph, was determined by comparing the amount of dissolved metal (at equilibrium) to the total amount of Cu and Zn (dissolved and undissolved) contained in each sample. Soluble metal levels plotted in Figures 1-7 represent the mean and standard deviation for each data set.

Generally, the percentage of soluble Cu dissociated from the brass ranged from 5 to 11% at all hardness levels (Figures 1 and 2). This dissociation was slightly greater (7-11%) in very soft and very hard water as opposed to soft and hard water (5-7%). The surface and sonicated samples attained the same percentage of Cu dissociation with the exception of the very soft samples (Figure 5). Equilibration time for the dissolved Cu occurred within 1-7 days for the sonicated samples, indicating a quick release of the Cu from the brass. For surface samples, the release of Cu was more gradual with equilibrium occurring within 7-14 days.

The amount of soluble Zn dissociated from the brass ranged from 6 to 8% for the soft, hard, and very hard samples and up to 32-60% for the very soft samples (Figures 3 and 4). Generally, twice as much Zn dissociation occurred from the sonicated samples as from the surface samples (Figure 6). Equilibration time for the dissolved Zn was similar to the Cu, occurring within 1-3 days for the sonicated samples versus 7-14 days for the surface samples.

Metal dissociation for the grenade samples was almost equal to the brass samples at the soft and hard water levels (Figure 7). The percentage of dissociation of dissolved Cu ranged from 5 to 6% for the surface and sonicated brass samples and 5 to 7% for the grenade. The percentage of Zn dissociation in the surface samples ranged from 6 to 7% (brass) versus

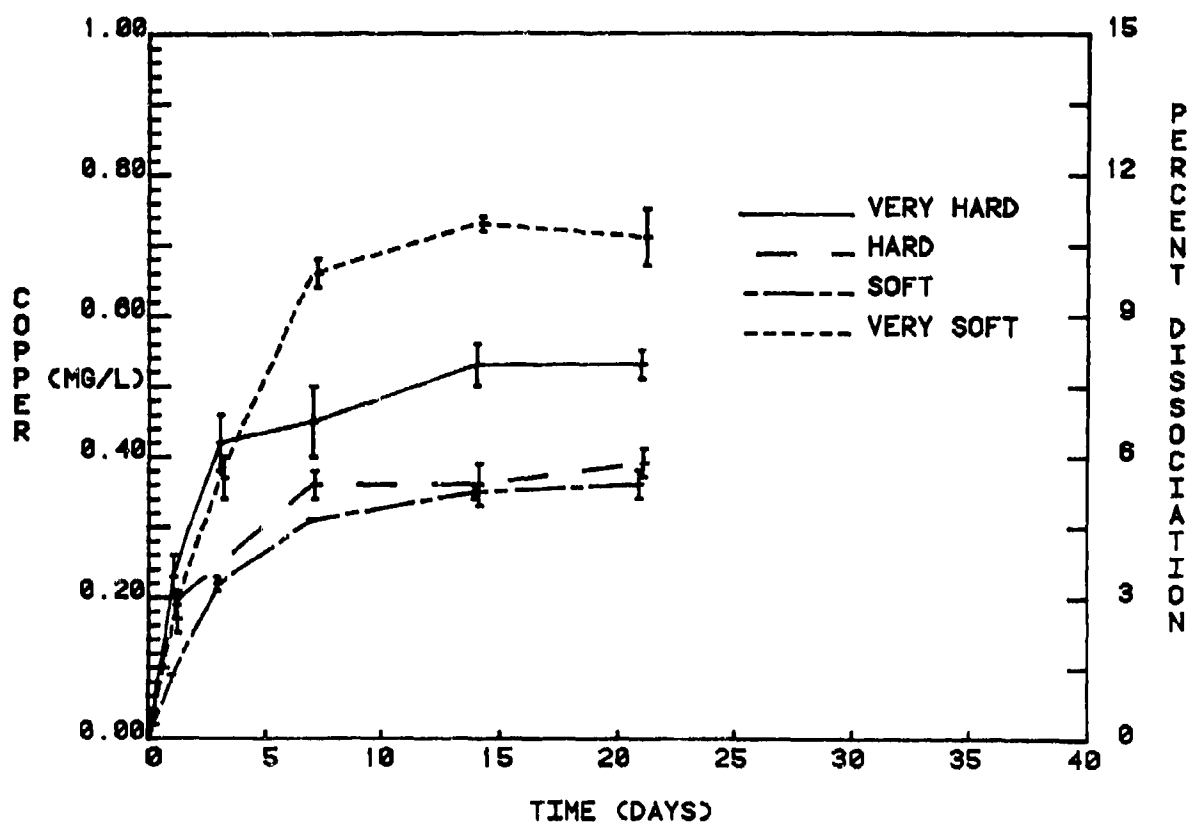


Figure 1. Brass Dissociation (Surface) Soluble Cu vs. Water Hardness.

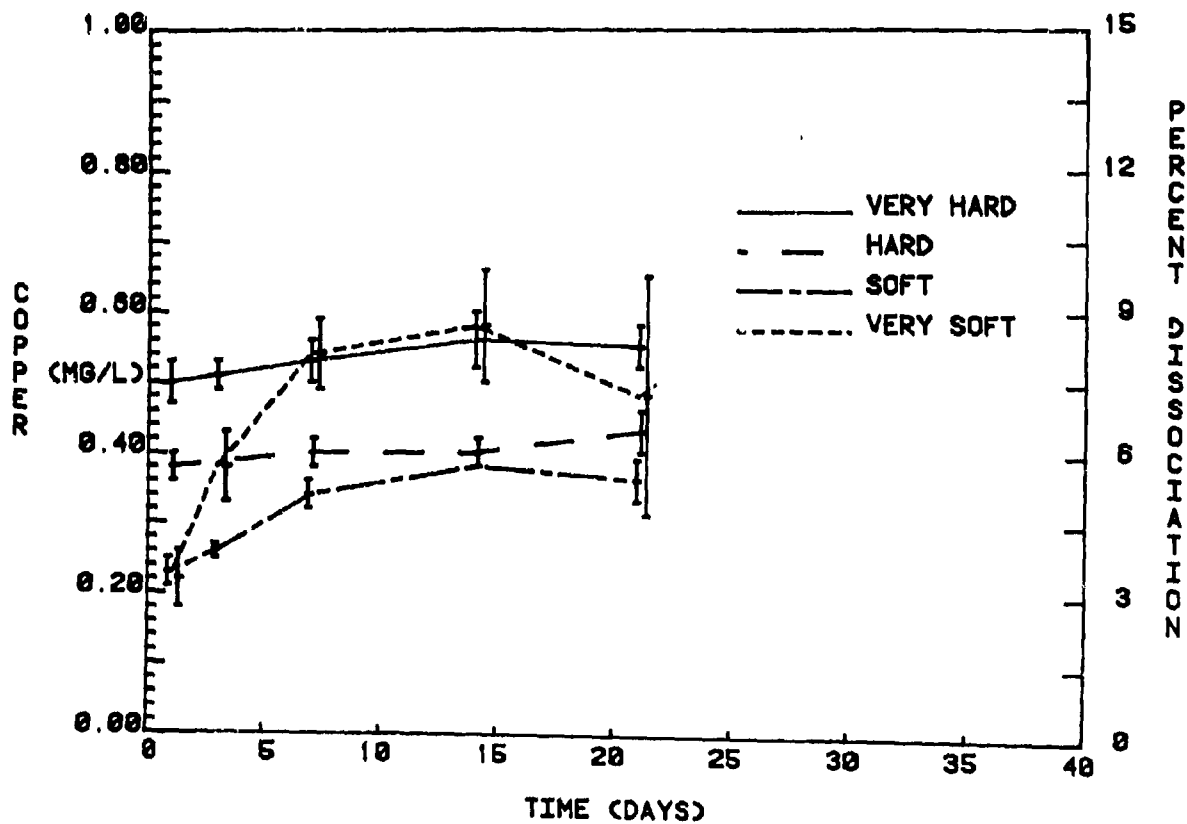


Figure 2. Brass Dissociation (Sonicated) Soluble Cu vs. Water Hardness.

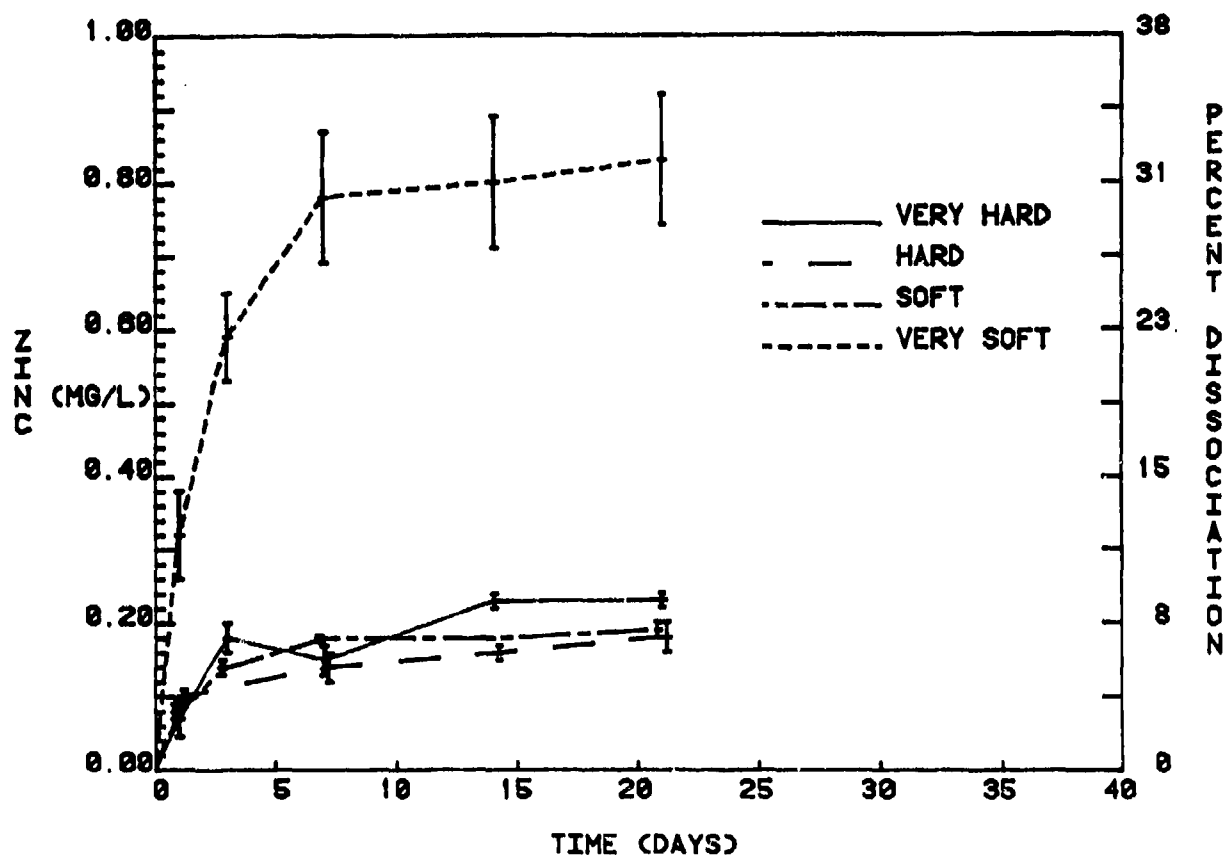


Figure 3. Brass Dissociation (Surface) Soluble Zn vs. Water Hardness.

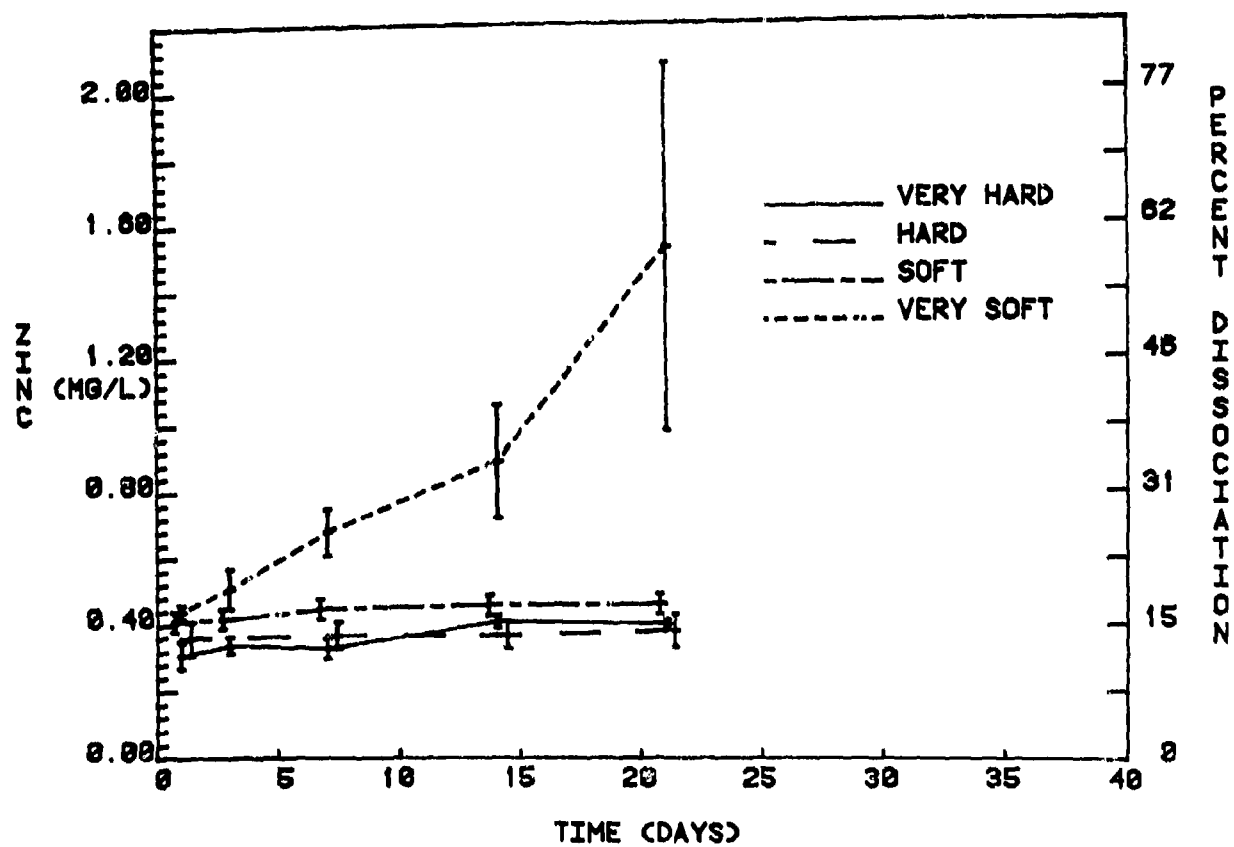


Figure 4. Brass Dissociation (Sonicated) Soluble Zn vs. Water Hardness.

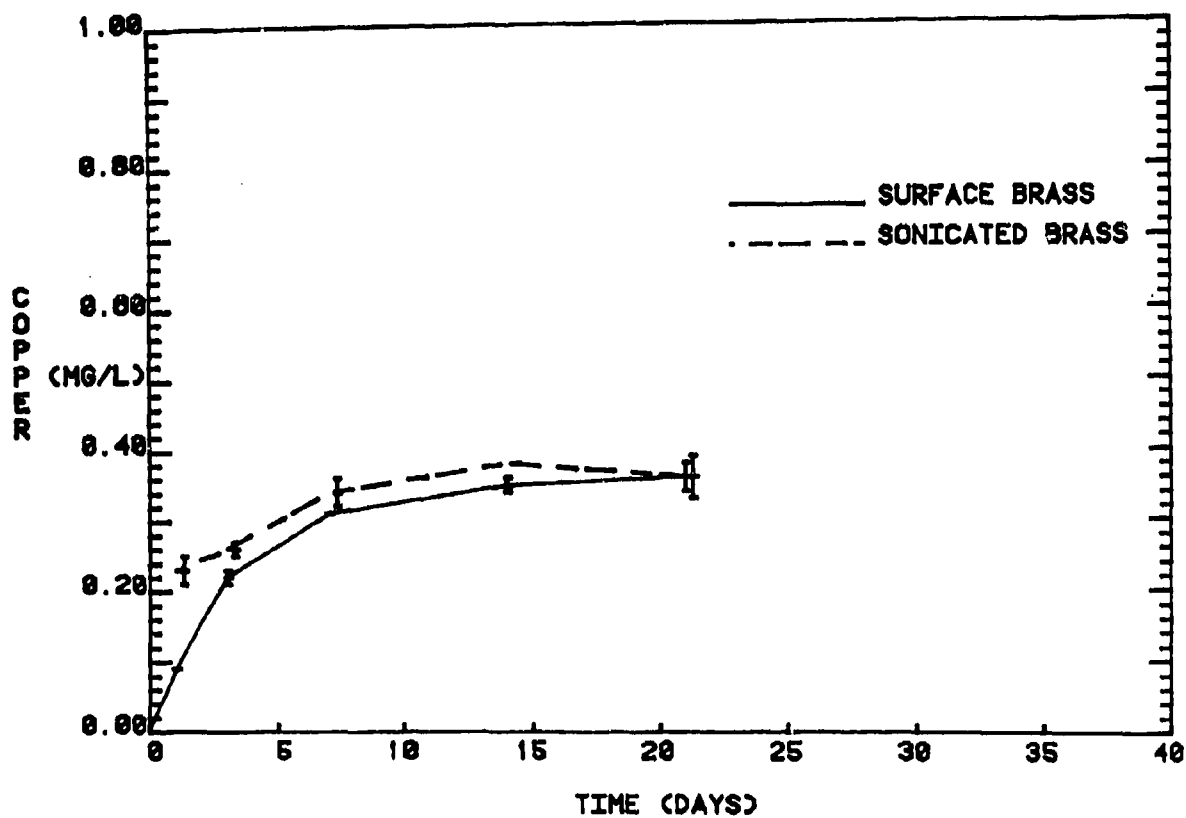


Figure 5. Surface Applied vs. Sonicated Brass Soluble Cu - Soft Water.

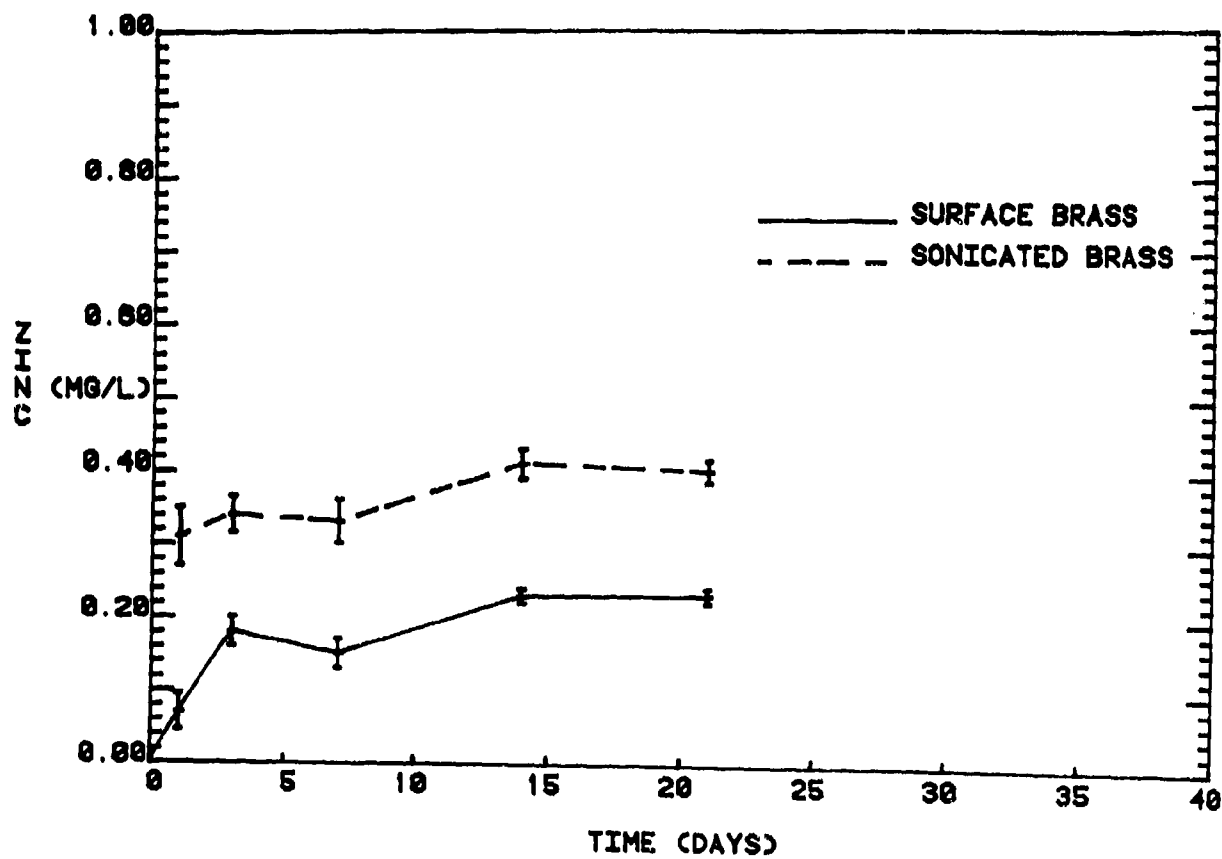


Figure 6. Surface Applied vs. Sonicated Brass Soluble Zn - Very Hard Water.

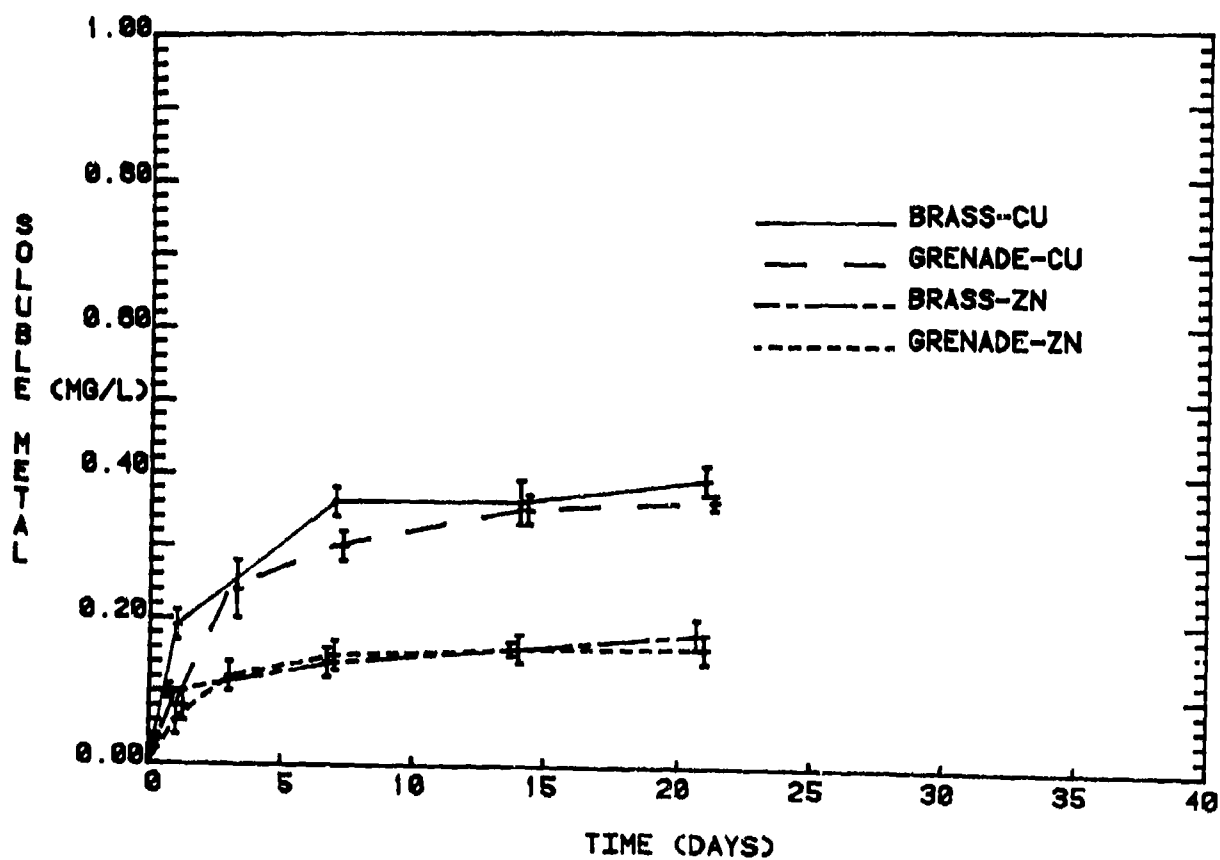


Figure 7. Dissociation of Brass vs. Grenade Soluble Metal in Soft Water.

6-10% (grenade). Sonicated brass samples had a range of 14-18% Zn dissociation versus 12-16% for the sonicated grenade samples.

The rate of soluble Cu and Zn moving from the surface applied brass into water was approximated using first-order kinetics (equations 1 and 2). These rates were determined from log-normal plots of soluble metal concentration ($C^\infty - C_t$) against time (days 0-7) with time on the linear axis (Figure 8). Each set of data (5 replicates) was plotted to determine the average half-life and kinetic rate of soluble Cu and Zn leaving the brass at each hardness level (Table 3).

$$\log (C^\infty - C_t) = Kt \quad (1)$$

where

C^∞ = dissolved metal conc at time infinity

C_t = dissolved metal conc at observed time t

$$K_1 = \ln 2 / t(1/2) \quad (2)$$

Kinetic results show the rate of soluble metal movement from the brass starting from day 0 up until day 7 (equilibrium). The effect of increasing the water hardness did not result in a uniform increase or decrease in the rate constants. However, both metals were calculated to have an estimated half-life of 1-3 days at all hardness levels. This indicates a fairly quick movement of soluble Cu and Zn from the brass. The fastest rate for Cu occurred in the very hard water while Zn moved fastest in the very soft water.

Results from the total ion analysis (sample 6) showed the relative amounts of total Cu and Zn present at the end of the study. At day 21, the brass samples showed a 100% recovery of total ions based on the initial Cu/Zn composition of the brass. The grenade samples showed a range of 86 (sonicated samples) to 98% (surface applied brass) recovered ions at day 21. During sonication, the Zn may have formed some complexes with other components in the grenade material that were not released during the acid digestion procedure.

Visual observations of the brass flakes during testing showed that the surface applied brass formed a thin, even coating on the water surface. However, particles from the grenade

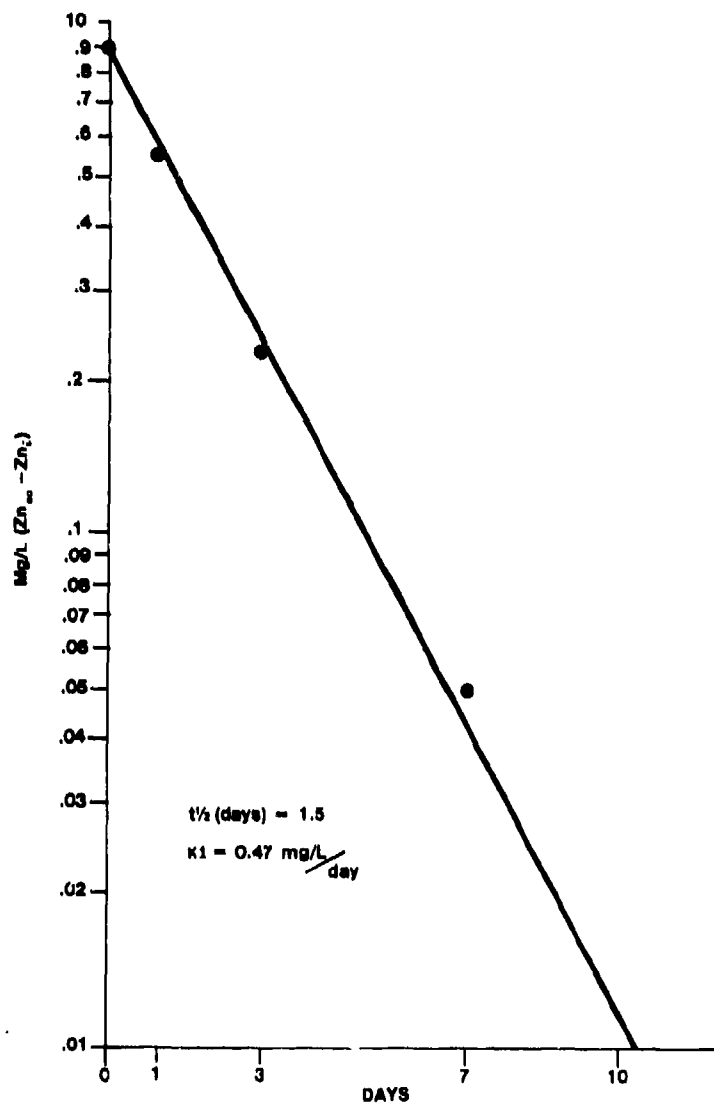


Figure 8. Kinetic Rate Determination of Zn Leaving the Brass in Very Soft Water.

Table 3. First-Order, Kinetic Approximations of Soluble Cu and Zn Leaving the Brass.

I. Dissolved Cu

Water Hardness	K1 (mg/L) (day-1) CV*	Half-life (days) CV*
Very Soft	.24 + .01 (4.3%)	2.86 + .12 (4.1%)
Soft	.24 + .02 (8.3%)	2.86 + .22 (7.8%)
Soft (Grenade)	.23 + .02 (8.2%)	3.0 + .27 (9.1%)
Hard (Grenade)	.31 + .04 (13.4%)	2.26 + .32 (14.2%)
Hard **	--- --- ---	--- --- ---
Very Hard	.46 + .06 (13.6%)	1.53 + .21 (13.9%)

II. Dissolved Zn

Water Hardness	K1 (mg/L) (day-1) CV*	Half-life (days) CV*
Very Soft	.45 + .06 (13.3%)	1.56 + .02 (12.6%)
Soft	.22 + .01 (4.0%)	3.11 + .12 (4.0%)
Soft (Grenade)	.22 + .02 (10.2%)	3.20 + .34 (10.5%)
Hard (Grenade)	.35 + .05 (14.7%)	2.04 + .36 (17.5%)
Hard **	--- --- ---	--- --- ---
Very Hard	.36 + .05 (12.3%)	1.94 + .25 (13.0%)

* Coefficient of Variation

** Insufficient data to compute kinetic rate of brass in hard water.

samples clumped together, and the coating was more patchy. These particles remained on the surface layer throughout the study. Sonicated brass flakes showed the opposite effect. Sonicating the brass caused a rapid breaking of the surface tension of the metal and allowed maximum metal-to-liquid contact in the aqueous media. This action resulted in a suspension of brass within the water column and also caused a majority of the material to sink to the flask bottom.

4. DISCUSSION

In natural waters, the dissociated Cu and Zn can readily react with a variety of other chemical species to form insoluble precipitates for soluble oxides, hydroxides, carbonates, and metal-organics.⁸ The concentration of these species will vary depending upon the chemical conditions (e.g., pH, hardness, and nutrient levels) of the aqueous system. Although the soluble metal species were not identified in this study, they can be predicted based on the previous work and modeling performed by Chakoumakos et al.,⁸ Andrew et al.,⁹ and Stiff.¹⁰ The most abundant forms of soluble Cu under tested conditions would probably consist of Cu (II) carbonate (CuCO_3) followed by Cu (II) hydroxide [$\text{Cu}(\text{OH})_2$] and decreased amounts of the ions Cu^{++} and CuOH^+ . Chakoumakos found that the amount of Cu^{++} present would vary due to variations in alkalinity and pH.⁸ For instance, the low alkalinity of the very soft water (Table 1) would probably cause an increase in Cu^{++} solubility. This may explain why the very soft water had the greatest dissolved Cu concentrations compared to the other levels of hardness (Figures 1 and 2). The most abundant forms of soluble Zn would probably result from the corrosion of brass to form Zn oxide. The Zn oxide would, in turn, hydrolyze to form ZnOH^+ and Zn^{++} . The formation of ZnOH^+ , Zn^{++} , and other soluble Zn species occurred to the largest extent in very soft water (Figures 3 and 4).

The dissociation of soluble Cu and Zn from the brass occurred quickly. Metal analysis on day 1 showed dissolved Cu levels ranging from 0.1 to 0.5 mg/L and soluble Zn levels ranging from 0.05 to 0.4 mg/L. These levels increased from 0.35 to 0.7 mg/L of dissolved Cu and 0.16 to 1.55 mg/L of dissolved Zn once a steady state was attained (1-7 days). The greatest dissociation of soluble Cu and Zn from the brass occurred in the very soft and very hard water.

A comparison between surface and sonicated samples showed the effect of aqueous mixing on metal dissociation.

Initially, sonicated samples had a significantly higher concentration of dissolved metals than the surface samples. However, from day 7-21, the surface and sonicated samples attained the same level of Cu dissociation. Mixing did have a greater influence on Zn dissociation. Soluble Zn levels in the sonicated samples were essentially double the concentration of the surface samples (Figure 6).

The rate of soluble Cu and Zn dissociated from the brass was estimated using first-order kinetics. In most cases, the data points correlated well with the calculated slope (K1), and a reasonable prediction of the rate constant and half-life could be made. However, this does not imply that a first-order reaction rate was responsible for the brass dissociation. The chemical transformation of the brass was primarily due to oxidation. However, hydrolysis reactions and the influence of other inorganic ions and complexes (Ca, Mg, CaCO_3) were also involved in the brass reaction scheme.

A prediction on the fate of the undissolved brass flakes in an aquatic system is based on visual observations of the surface applied and sonicated brass samples. An introduction of brass would initially coat the water surface layer. If the mixing conditions of an aquatic system are slow, the brass would remain on the surface layer for an extended period of time. In this study, the surface applied brass remained on the water surface for over 2 months. A vigorous mixing of an aquatic system due to the effects of wind, currents, and upwelling, would probably cause the brass to sink to the sediment layer as did the sonicated samples. The presence of suspended particles in the water column would also contribute to the transport of brass particles to the sediment.

The toxicological effects of the brass in an aquatic system can be predicted based on the dissociation study. Any toxic response (resulting from brass' quick dissociation into soluble Cu and Zn) from marine organisms would occur soon after brass' introduction into natural waters. The soluble Cu and Zn species that have a demonstrated toxicity to marine organisms include Cu^{++} , CuOH^+ , $\text{Cu}_2(\text{OH})_2^{++}$ and Zn^{++} , ZnOH^+ .^{8,11} Of these species, Cu^{++} , Zn^{++} and ZnOH^+ would most likely occur in the hard waters tested. The greatest dissociation and subsequent toxicity would occur at the very soft water levels. Because a large percentage of the surface applied brass powder remained on the water surface, the powder could affect the filter feeding mechanism of neustonic organisms. Brass particles suspended

within the water column or absorbed onto suspended particles can also impart toxicity when ingested by aquatic organisms.

5. CONCLUSIONS

The dissociation of brass into soluble Cu and Zn occurs quickly. First-order, kinetics approximations of the data show a 1-3 day half-life of soluble metal leaving the brass in the tested water hardness levels. Any associated toxicity of the brass to aquatic organisms should occur soon after the brass enters the aqueous environment.

Mixing the brass into the test water as opposed to applying it on the water surface accelerates the release of soluble Cu and Zn. However, surface and sonicated brass attained the same level of Cu dissociation once equilibrium was reached. The effects of mixing caused twice as much Zn to dissociate from the sonicated brass at equilibrium as opposed to the surface applied brass.

The greatest dissociation of brass into soluble metal occurs in the very soft water, which shows a significant degree of brass dezincification. The very hard water also shows a slightly increased amount of Cu dissociation. Otherwise, the soft, hard, and very hard water were comparatively the same for soluble metal release.

Metal dissociation for the grenade launched brass was tested in the soft and hard water only and was essentially the same as the brass dust.

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